PF040161

PF040161 (JP2002352961) ON 7476

(19) Japanese Patent Office (JP)
(12) Publication Patent Official Report (A)
(11) Publication number: 2002-352961
(43) Date of publication of application: 06.12.2002
(51) Int.Cl. H05B 33/22 H05B 33/14
(21) Application number: 2001-157544
(22) Date of filing: 25.05.2001
(71) Applicant: Toray IND INC
(72) Inventor: Takano Akiko, Tominaga Takeshi, Asahi Noboru

(54) Title of the invention: Organic electroluminescent device

(57) Abstract:

Problem to be solved: To provide organic field light-emitter, which has high luminescence efficiency, low drive voltage, and high durability.

Solution: In the organic field light-emitter, including thin film layer, which includes an emission layer and electron transport layer, which at least consist of an organic compound, and a second electrode formed on the thin film layer, on a first electrode formed on a substrate, the electronic transport layer consists of an organic compound having a molecular weight of 400 or more, donor type impurities are doped, at least in one part of the electron transport layer, and the organic compound has a site, in which the chelate coordination of donor type impurities is possible.

[Claims]

[Claim 1] In the organic electroluminescence equipment containing the second electrode formed on the first electrode formed on the substrate on the thin film layer containing the luminous layer and electron transport layer which consist of an organic compound at least, and the thin film layer, said electron transport layer is organic electroluminescence equipment characterized by for molecular weight consisting of 400 or more organic compounds, and for the donor type impurity is doped by said a part of electron transport layer at least, and having the site which said organic compound can chelate coordination of a donor type impurity.

[Claim 2] Organic electroluminescence equipment according to claim 1 characterized by an organic compound having nitrogen content heterocycle structure.

[Claim 3] Organic electroluminescence equipment according to claim 1 characterized by an organic compound having a pyridine frame.

[Claim 4] Organic electroluminescence equipment according to claim 1 with which an organic compound is characterized by having 1, 10-phenanthroline frame.

[Claim 5] Organic electroluminescence equipment according to claim 1 with which an organic compound is characterized by having two or more 1, 10-phenanthroline frame.

[Claim 6] Organic electroluminescence equipment according to claim 1 characterized by that a donor type impurity is alkali metal.

[Claim 7] Organic electroluminescence equipment according to claim 1 characterized by that the sum total

thickness of an electron transport layer and a luminous layer is 50nm or more.

[Detailed description of the invention]

[0001]

[Field of the invention] This invention is equipment that can change electrical energy into light, and relates to organic electroluminescence equipment available in the field of a display device, a flat-panel display, a back light, lighting, an interior, an indicator, a signboard, an electrophotography machine, a lightwave signal generator, etc.

[0002]

[Description of the prior art] Research of the organic laminating thin film luminescence equipment which emits light in case the electron hole poured in from the first electrode (anode plate) formed on the substrate and the electron poured in from the second electrode (cathode) recombine within the organic fluorescent substance inserted into two poles is done actively in recent years. Multicolor luminescence by this equipment choosing a thin shape, high brightness luminescence under low driver voltage, and a fluorescence ingredient is the description.

[0003] It was shown for the first time by C.W.Tang and others of Kodak that organic electroluminescence equipment emits light in high brightness (913 Appl.Phys.Lett. 51 (12) 21 p. 1987). The typical configuration of the organic electroluminescence equipment which Kodak presented prepared Mg:Ag one by one on the ITO glass substrate as the tris (8-quinolinolato) aluminum which is the diamine compound of electron hole

transportability, and a luminous layer, and also had electronic transportability, and cathode, and 1000 candelas/square meter green luminescence was possible for it at about 10V driver voltage. Fundamentally, current organic electroluminescence equipment has followed the configuration of Kodak, and is having structure where the laminating of the thin film layer and the second electrode which contain the first electrode and a luminous layer on a substrate was carried out one by one. Although the configuration of a thin film layer may be the monolayer structure of only a luminous layer, many are two or more laminated structures which prepared the electron hole transporting bed and the electron transport layer.

[0004] It is necessary to fill improvement in luminous efficiency, lowering of driver voltage, and improvement in endurance to organic electroluminescence equipment. If luminous efficiency is low, the consumed electric power for the output of the image which requires high brightness becoming impossible, and outputting desired brightness will increase. In order to raise luminous efficiency, there is a method of using cross protection with the reflected light from cathode, but in the optimum conditions, since a thin film layer is thick, driver voltage will go up. On the other hand, although it is desirable for the improvement in endurance to use a compound with a high glass transition point, generally, the high compound of a glass transition point has the inclination for electric resistance to be also high, and driver voltage will go up. Also, if thickness of a thin film layer is thickened in order to raise the endurance over the leak and continuation actuation by foreign matter mixing, driver voltage will go up in connection with it. As

mentioned above, when it was going to raise luminous efficiency and endurance, there was a problem that driver voltage went up.

[0005]

[Problems to be solved by the invention] This invention solves the problems of this conventional technique, that are high luminous efficiency and low driver voltage, and aims at offering the organic electroluminescence equipment of high endurance.

[0006]

[Means for solving the problem] In the organic electroluminescence equipment containing the second electrode formed on the first electrode with which this invention was formed on the substrate on the thin film layer containing the luminous layer and electron transport layer which consist of an organic compound at least, and the thin film layer Molecular weight consists of 400 or more organic compounds, the donor type impurity is doped by said a part of electron transport layer at least, and said electron transport layer is organic electroluminescence equipment with which said organic compound is characterized by having the site in which chelate coordination of a donor type impurity is possible.

[0007]

[Embodiment of the invention] Next, the organic electroluminescence equipment by this invention is explained.

[0008] Doping of the donor type impurity in this invention makes easy carrier impregnation on the electric conduction disposition of an electron transport layer. In order to raise electronic transport capacity, a donor type impurity is

doped to an electron transport layer. As for the donor type impurity in this invention, alkali metal, an alkaline earth metal, the amino compound, ammonia, a tetrathiafulvalene derivative, a tetra-serena full baren derivative, etc. are mentioned. Especially, vacuum evaporationo in a vacuum is easy, it is easy to be spread in an organic thin film, alkali metal in a low work function, such as a lithium with the large effectiveness of the improvement in electronic transport ability, sodium, a potassium, a rubidium, and caesium, and alkaline earth metal, such as magnesium, calcium, strontium, and barium, are desirable, and the smallest caesium has alkali metal, especially a more desirable work function among all elements.

[0009] As an electronic transportability ingredient, it is required to convey the electron from cathode efficiently, electronic injection efficiency is high, and it is desirable to convey the poured-in electron efficiently. For that purpose, an electron affinity is large, moreover electron mobility is large, it excels in stability further, and to be the matter which the impurity used as a trap cannot generate easily at the time of manufacture and an activity is demanded. The compound molecular weight excelled compound in thermal resistance greatly as an ingredient excellent in endurance is desirable. When carrying out the laminating especially of the thickness thickly, since it crystallizes and membraneous quality tends to deteriorate, the compound of low molecular weight has a with a molecular weight of 400 or more which maintains stable membraneous quality desirable compound, and it is more desirable that it is 600 or more.

[0010] Also, it is not desirable in order that a donor type impurity may not act on the compound that has already carried out complexing by intramolecular effectively, when doping a donor type impurity. The compound which a donor type impurity commits effectively is a compound which has the site that can configurate a donor type impurity. The site that can be configurated points out the supply site of the unshared electron pair which a compound can configurate in other atoms and molecules. Since it is easy to stabilize rather than an interaction with a single seat coordination site even if chelate coordination of the donor type impurity is not carried out actually when the coordination becomes the structure in which chelate coordination is possible, the membraneous improvement effect of electronic transport ability not only improving more effectively but a thin film is also large. Chelate coordination structure is the method of coordination that the supply site of two or more unshared electron pairs configurates in one atom or molecule simultaneously, and forms a ring structure.

[0011] Atoms, such as nitrogen, oxygen, and sulfur, a carbon unsaturated bond, a delocalization carbocyclic atomic group, etc. as the atom which is an electron pair donor, or an atomic group. These can all supply an electron pair to the orbit of the empty of an atom or a molecule. Therefore, as a compound which has the site in which chelate coordination is possible, the compound containing derivatives, such as dithiocarbamic acid which has derivatives, such as diphosphine which has derivatives, such as a diether which has derivatives, such as diamine

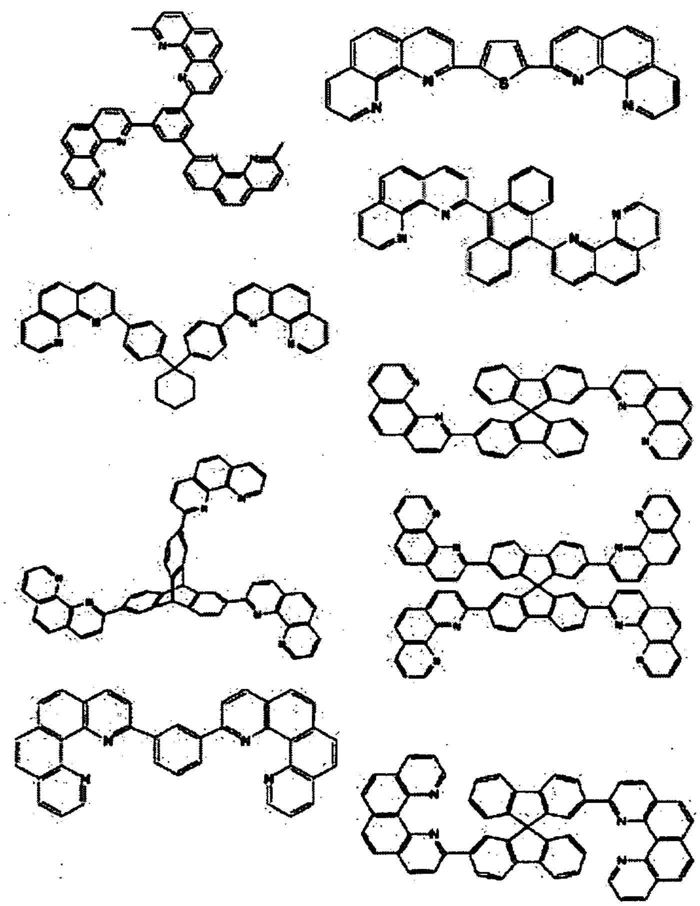
which has two or more nitrogen atoms, triamine, a bipyridine, and a porphyrin, and two or more oxygen atoms, an acetylacetone, a carboxylic acid, and oxalic acid, and two or more sulfur atoms and two or more kinds of other different electron pair supply atoms etc. can be mentioned. In these, the coordination by the unshared electron pair of a nitrogen atom has a strong interaction, and is desirable also in a large point.

[0012] The compound with which the same nitride also contains the pyridine which is a nitrogen content heterocyclic compound, pyrazine, a pyrimidine, pyridazine, triazine, tetrazine, pentagin, oxazine, diazine, thiazin, thiadiazin, pyrrole, oxazole, oxadiazole, thiazole, thiadiazole, imidazole, triazole, etc. rather than an amine compound from the point of electronic transportability is desirable. Especially, the compound which contains a pyridine from the stability of coordination is desirable, and the compound in which N atom of two pyridines rings, such as a compound that has two or more pyridine rings, for example, 1, 8-nafuchilysine, 2, 2'-bipyridine, can form 4 - 7 membered-ring by chelate coordination is more desirable as a compound which has the structure in which chelate coordination is possible. The compound which has the 2, 2'-bipyridine frame which can form a five-membered ring from the field of the stability of chelate coordination is desirable, and the compound which has 1, 10-phenanthroline frame especially is desirable. The compound with which two or more 1, 10-phenanthroline frames are contained from the point of the membraneous stability at the time of thin film formation or electronic transportability is more desirable.

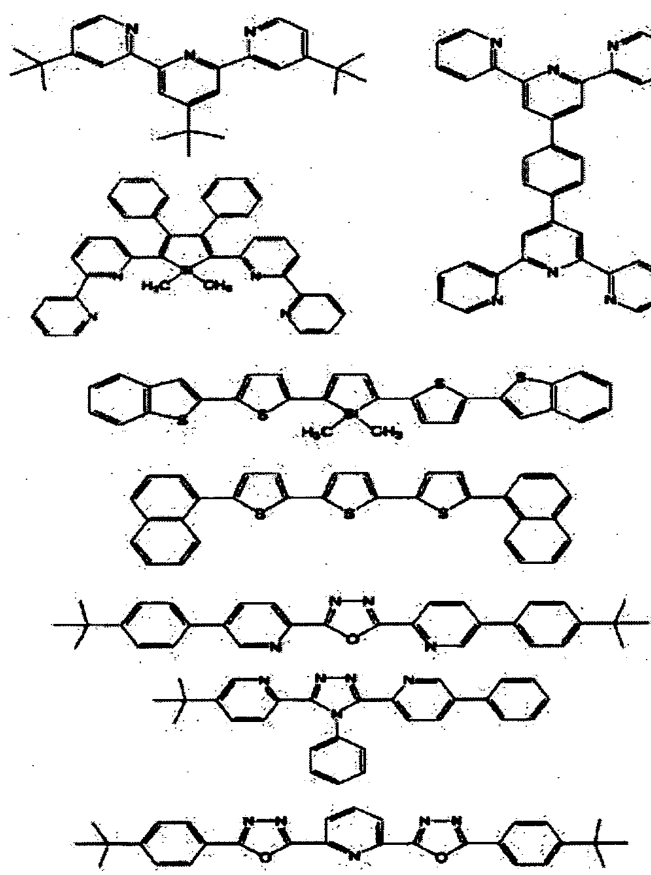
[0013] It is not limited especially although the compound shown in formula 1 is mentioned as matter which fulfills such conditions. an electronic transport ingredient which is different although it is used even when these electronic transport ingredients are independent, and a laminating or it does not matter even if it mixes and uses it.

[0014]

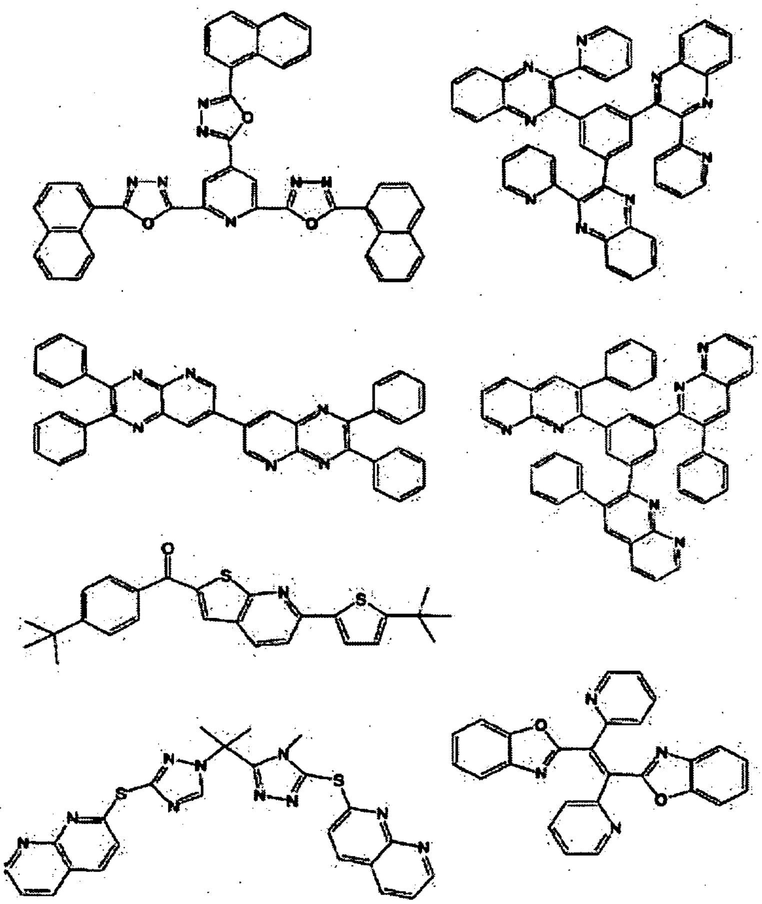
[Formula 1]



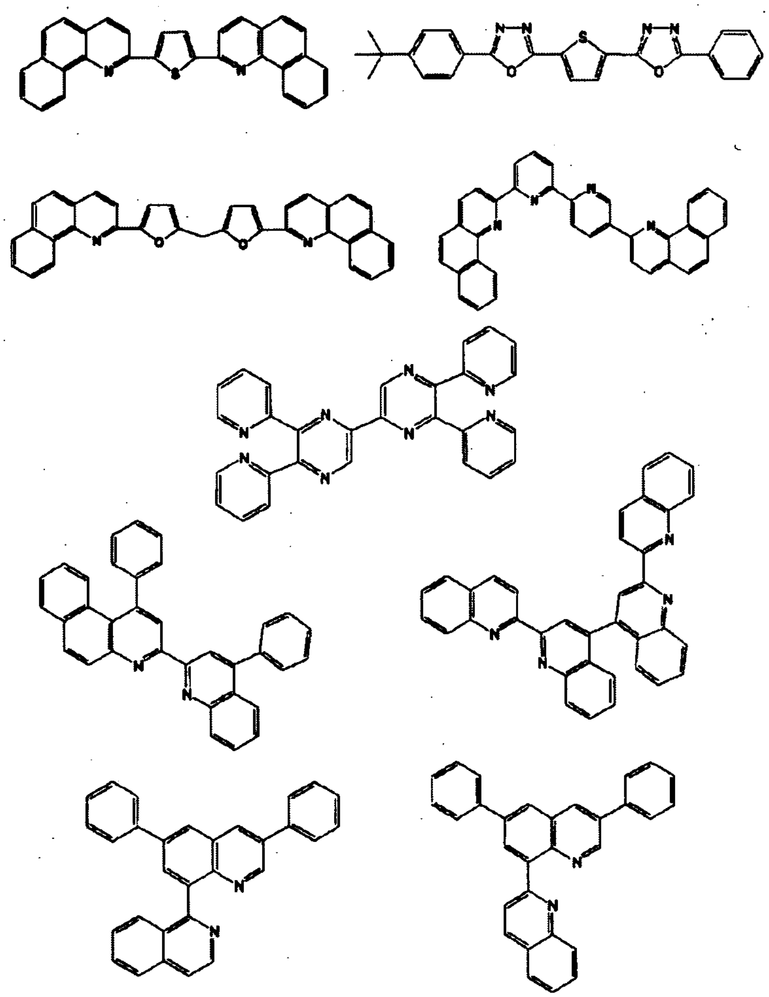
[0015] [Formula 2]



[0016] [Formula 3]



[0017] [Formula 4]



[0018] Although there is a method of using cross protection in order to raise luminous efficiency, this adjusts the phase of the light directly emitted from a luminous layer, and the light reflected in cathode, and raises th e ejection effectiveness of light. Although these optimum conditions change according to the luminescence wavelength of light, the sum total thickness of an electron transport layer and a luminous layer may be set to 50nm or more, and, in red long wavelength luminescence, they may become an about 100nm thick film.
[0019] When the thickness of such a thin film layer is thick, especially the approach of doping a donor type impurity to an electron transport layer, and raising electronic transport ability demonstrates effectiveness. When the sum total thickness of an electron transport layer and a luminous layer is 50nm or more, it is used preferably, and in 70nm or more, it is used more preferably.
[0020] Although a part of electron transport layer or all whichever are sufficient as the thickness of the electron transport layer to dope, its one where the thickness doped, so that the whole thickness is thick is also thicker is good. When doping to a part, it is desirable to prepare a doping layer in an electron transport layer / cathode interface at least, and the effectiveness of low battery is acquired doping near an interface.
On the other hand, if a donor type impurity is doped by the luminous layer, since the adverse effect to which luminous efficiency is reduced may be done, it is desirable to prepare a non dope layer 5nm or more in a luminous layer / electron transport layer interface.

[0021] Although suitable doping concentration changes also with thickness of an ingredient or a doping layer, the range of the mole ratios 100:1-1:100 of an organic compound and a donor type impurity is desirable, and 10:1-1:10 are more desirable. When there is two or more number of the sites in which chelate coordination is possible, it is desirable to set the ratio of the donor impurity around a coordination site to 10:1-1:10.

[0022] In order that the first electrode and the second electrode may have a role for supplying current sufficient for luminescence of a component and may take out light, it is desirable to be transparence or for at least one side to be translucent. Usually, the first electrode formed on a substrate is used as a transparent electrode, and let this into an anode plate and let the second electrode be cathode.

[0023] The ingredient used for the first electrode has especially the desirable thing for which ITO glass and Nesa glass are used, although especially conductive polymers, such as inorganic conductivity matter, such as metals, such as conductive metallic oxide, such as tin oxide, indium oxide, and a tin oxide indium (ITO) zinc oxide indium (IZO), or gold, silver, and chromium, copper iodide, and copper sulfide, the poly thiophene, polypyrrole, and the poly aniline, etc. are not transparence or the thing limited if translucent in order to take out light. Although it is not limited since resistance of a transparent electrode just supplies sufficient current for luminescence of a component, from a viewpoint of the power consumption of a component, it is desirable that it is low resistance. For example, since supply of the substrate of 10 O/? extent is also attained, especially the thing for which the substrate of

the low resistance below 20 O/? is used is desirable if it is an ITO substrate below 300 O/? , it will function as a component electrode current. Although the thickness of ITO can be chosen as arbitration according to resistance, it is usually used among 100-300nm in many cases. Especially as for the ITO film formation approach, electron beam vacuum deposition, the sputtering method, a chemical reaction method, etc. do not receive a limit.

[0024] Since a glass substrate should just have sufficient thickness to use alkali free glass, etc., and for thickness also maintain a mechanical strength, it is enough if there is 0.5mm or more. About the construction material of glass, since the direction with little elution ion from glass is good, alkali free glass is more desirable, but since the soda glass which gave barrier coating sealant, such as SiO_2, is also marketed, this can be used.

[0025] The ingredient used for the second electrode will not be limited especially if it is the matter that can pour an electron into a luminous layer efficiently. Generally, an alloy, a multilayer laminating, etc. of metals, such as platinum, gold, silver, copper, iron, tin, aluminum, and an indium, or these metals, and low work function metals, such as a lithium, sodium, a potassium, calcium, and magnesium, are desirable. Especially as a principal component, aluminum, silver, and magnesium are desirable from fields, such as membranous stability and luminous efficiency, in an electric resistance value or the ease of producing a film.

[0026] Although resistance heating vacuum evaporation, electron beam evaporation, sputtering, a molecule laminated layers method, a coating method, etc. are

mentioned and the formation approach of a thin film layer is not limited especially, resistance heating vacuum evaporation and its electron beam evaporation are usually desirable in respect of a property.

[0027] It is required to convey the electron hole from a positive electrode efficiently as an electron hole transport ingredient in inter-electrode that was able to give electric field, hole-injection effectiveness is high, and it is desirable to convey the poured-in electron hole efficiently. It has ionization potential suitable for that purpose, and moreover, hole mobility is large, and is further excellent in stability, and to be the matter which the impurity used as a trap cannot generate easily at the time of manufacture and an activity is demanded. As matter which fulfills such conditions, although not limited especially, known electron hole transport ingredients, such as triphenylamine derivatives, such as TPD, m-MTDATA, and a-NPD, a bis-carbazolyl derivative, a pyrazoline derivative, a stilbene system compound, a heterocyclic compound represented by a hydrazone system compound and the phthalocyanine derivative, a polyvinyl carbazole, and polysilane, can be used. An electron hole transport ingredient which is different although it is used even when these electron hole transport ingredients are independent, and a laminating or it does not matter even if it mixes and uses it.

[0028] Luminescent material may be any also in the combination of a host ingredient and host ingredient and a guest ingredient. Moreover, the guest ingredient may be contained in the whole host ingredient, may be contained selectively, or may be any. The laminating may be carried out, it may distribute, or guest ingredients may be any.

[0029] Condensed-ring derivatives with which luminescent material was specifically known as an emitter for some time, such as an anthracene and a pyrene, Metal chelation oxynoid compounds including tris (8-quinolinolato) aluminum, Bis-styryl derivatives, such as a bis-styryl anthracene derivative and a benzene derivative, A tetra-phenyl butadiene derivative, a coumarin derivative, an oxadiazole derivative, by a pyrrolo pyridine derivative, a peri non derivative, the cyclopentadiene derivative, the oxadiazole derivative, the thiadiazolo pyridine derivative, and the polymer system. It is not limited especially although a polyphenylene vinylene derivative, a poly para-phenylene derivative, the poly thiophene derivative, etc. can be used.
[0030] Although especially the dopant ingredient added to luminescent material is not limited, a known dopant ingredient can be used. Condensed-ring derivative that are specifically known, such as perylene and rubrene, Quinacridone derivative, phenoxazone 660, DCM1, and peri non, a coumarin derivative, a pirometen (diazaindacene) derivative, cyanine dye, etc. can use it as it is.
[0031] Although the ingredient used for the above electron hole transporting bed and a luminous layer can form each class independently As a giant-molecule binder, a polyvinyl chloride, a polycarbonate, polystyrene, Pori (N-vinylcarbazole), polymethylmethacrylate, poly butyl methacrylate, Polyester, polysulfone, polyphenylene oxide, polybutadiene, Hydrocarbon resin, ketone resin, phenoxy resin, a polyamide, ethyl cellulose, Solvent fusibility resin, such as vinyl acetate, ABS plastics, and polyurethane resin,

it is also possible to distribute hardenability resin, such as phenol resin, xylene resin, petroleum resin, a urea resin, melamine resin, an unsaturated polyester resin, alkyd resin, an epoxy resin, and silicone resin, etc., and to use.

[0032] Moreover, the above technique can be applied when it is the full color or display which consists of two or more luminescent color and in which a multicolor display is possible.

[0033]

[Example] This invention is not limited by these examples, although an example and the example of a comparison are given and this invention is explained next.

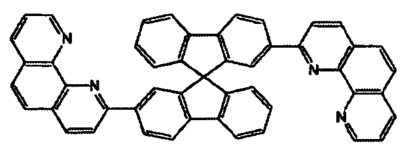
[0034] After cutting the glass substrate on which 120nm of ITO transparence electric conduction film was made to deposit by the example 1 sputtering method to 38x46mm, etching clearance of the garbage of ITO was carried out. After cleaning the obtained substrate ultrasonically for 10 minutes with alkali-cleaning liquid, ultrapure water washed. Just before producing a component, 1-hour UV / ozonization of this substrate were done, it installed in the vacuum evaporator, and it exhausted until the degree of vacuum in equipment was set to $5x10^{-4}$ or less Pa. With the resistance heating method, the laminating of the mixture of a guest ingredient (DCJTB) and host ingredient tris (8-quinolinolato) aluminum (Alq_3) was first vapor-deposited 60nm (CuPc) of copper phthalocyanines and made 10nm and a degree to the thickness of 25nm as a luminous layer continuously in N, N'-G (naphthalene-1-IRU)-N, N'-diphenyl-benzidine (NPD) as an electron hole transport ingredient. The guest could be 1 % of the weight to the host. Next, as an electron transport layer, vapor

codeposition of the electronic transport ingredient (ETL-1) and caesium which are shown in formula 5 was carried out at about 3:1 rate by the mole ratio, and the laminating was carried out to the thickness of 70nm. This molecular weight of electronic transport ingredient ETL-1 is 673. Furthermore, the electron transport layer front face was put to the steam of caesium, and was doped. It equipped with the mask for the second electrode, 150nm of aluminum was vapor-deposited, and it considered as cathode.

[0035] Thus, when the produced light emitting device was made to emit light with the current density of 4 mA/cm^2, in luminescence brightness, 102 cd/ m^2 and driver voltage emitted light by 4.8V, and luminous efficiency emitted light by 1.7 lm/W. When continuation actuation of this component was carried out by initial brightness 200 cd/ m^2, brightness did not reduce 1000 hours after by half.

[0036]

[Formula 5]



ETL-1

[0037] Vapor codeposition of the lithium was carried out to example 2 electron transport layer, the front face was put and doped with the steam of lithium, and also the component was produced like the example 1. When this component was made to emit light with the current density of 4 mA/cm2, in luminescence brightness, 95 cd/m^2 and driver voltage emitted light by 5.5V, and luminous efficiency emitted light by 1.4 lm/W. When continuation

actuation of this component was carried out by initial brightness 200 cd/m^2, brightness did not reduce 1000 hours after by half.

[0038] Thickness of example 3 electron transport layer was set to 20nm, and also the component was produced like the example 1. When this component was made to emit light with the current density of 4 mA/cm^2, in luminescence brightness, 80 cd/m^2 and driver voltage emitted light by 4.0V, and luminous efficiency emitted light by 1.6 lm/W. Although brightness did not reduce 1000 hours after by half when continuation actuation of this component was carried out by initial brightness 200 cd/m^2, one of four elements short-circuited 400 hours after.

[0039] The laminating of the electron transport layer was carried out without doping example of comparison 1 caesium, and also the component was produced like the example 1. When this component was made to emit light with the current density of 4 mA/cm^2, in luminescence brightness, 82 cd/m^2 and driver voltage emitted light by 7.8V, and luminous efficiency emitted light by 0.8 lm/W. When continuation actuation of this component was carried out by initial brightness 200 cd/m^2, brightness was halved 800 hours after.

[0040] As example of comparison 2 electron transport layer, vapor codeposition of bathocuproine and the caesium was carried out at about 3:1 rate by the mole ratio, and also the component was produced like the example 1. When this component was made to emit light with the current density of 4 mA/cm^2, in luminescence brightness, 59 cd/m2 and driver voltage emitted light by 4.2V, and luminous efficiency emitted light by 1.1 lm/W. When

continuation actuation of this component was carried out by initial brightness 200 cd/m^2, brightness was halved 600 hours after.

[0041] As example of comparison 3 electron transport layer, vapor codeposition of the caesium was carried out to Alq3 at about 3:1 rate by the mole ratio, and also the component was produced like the example 1. When this component was made to emit light with the current density of 4 mA/cm^2, in luminescence brightness, 75 cd/m^2 and driver voltage emitted light by 5.6V, and luminous efficiency emitted light by 1.1 lm/W. When continuation actuation of this component was carried out by initial brightness 200 cd/m^2, brightness was halved 750 hours after.

[0042] As example 5 electron transport layer, 15nm of non dope layers of ETL-1 was prepared, next, 55nm vapor codeposition of the caesium was carried out to ETL-1 at about 3:1 rate by the mole ratio, and also the component was produced like the example 1. When this component was made to emit light with the current density of 4 mA/cm^2, in luminescence brightness, 118 cd/m^2 and driver voltage emitted light by 5.0V, and luminous efficiency emitted light by 1.9 lm/W. When continuation actuation of this component was carried out by initial brightness 200 cd/m^2, brightness did not reduce 1000 hours after by half.

[0043]

[Effect of the Invention] By this invention, it is high luminous efficiency and low driver voltage, and the organic electroluminescence equipment of high endurance can be offered.